

PATENT SPECIFICATION

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(54) METHOD FOR PRODUCING A SHAPED ARTICLE OF A POLY-1,3,4-OXADIAZOLE RESIN HAVING IMPROVED PROPERTIES

(71) We, THE FURUKAWA ELECTRIC COMPANY LIMITED, a Japanese corporation, of 6-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for producing a shaped-article of a poly-1,3,4-oxadiazole resin having improved properties by wet-shaping process from a solution of said resin in concentrated sulfuric acid.

Recently, poly-1,3,4-oxadiazole resins have been developed as low-cost resins having a high heat resistance and many other excellent properties. Various methods for synthesis of these resins are known, for example, as follows.

(A) J. Polymer Sci., A3 45 (1965) discloses that said poly-1,3,4-oxadiazole resin is produced by reacting an aromatic dibasic acid or a derivative thereof with hydrazine or a salt thereof in fuming sulfuric acid or a polyphosphoric acid.

(B) U.S. Patent 3,238,183, J. Polymer Sci., A2 1157 (1964) discloses that an aromatic dibasic acid halide may be reacted with hydrazine or an aromatic dibasic acid dihydrazide in the presence of an acid acceptor to produce a polyhydrazide, which is converted into poly-1,3,4-oxadiazole by heating.

(C) Makromol. Chem., 44—6 388 (1961) discloses that a bistetrazole derived from an aromatic dibasic acid may be reacted with an aromatic dibasic acid halide in the presence of an acid acceptor to produce poly-1,3,4-oxadiazole.

(D) U.S. Patent 3,644,297, British Patent 1,252,508 and German Patent 1,902,591 discloses that an N-alkylhydrazide-1,3,4-oxadiazole copolymer is produced by reacting poly-1,3,4-oxadiazole with an alkyl sulfate in fuming or concentrated sulfuric acid.

The inventors have proposed in German Patent Application 1,769,151 laid open for

public inspection and British Patent 1,252,508 a method for forming a solution of poly-oxadiazole resins in concentrated sulfuric acid into shaped articles by wet-shaping process in which said solution is coagulated in a bath containing, for example, 10 to 68 weight % aqueous sulfuric acid. The method has various advantages for working on a commercial basis.

A shaped article, for example, a fiber, a film or an impregnated material, formed of a polyoxadiazole resin obtained in the above-mentioned process, has various excellent properties and especially that the tensile properties of said resin containing a 1,3,4-oxadiazole ring do not deteriorate even when heated at high temperature, for example, at 300° C. for 10 hours.

It has been found, however, that a shaped article of said resin containing a 1,3,4-oxadiazole ring has a poor dimensional stability, high water and moisture absorption as compared with those generally obtained by wet-shaping process and that it also has a poor light resistance. It has also been found that although it has a high heat resistance as above mentioned, if it is kept for a long time at a relatively low temperature at which it is often used, for example, 150—200° C., its excellent properties are gradually degraded. It is a serious problem in the practical use of a shaped article of a poly-1,3,4-oxadiazole resin.

An object of the present invention is to obviate or mitigate the above-mentioned drawback and to provide a method for producing a shaped article of a poly-1,3,4-oxadiazole resin having improved properties.

The inventors have studied diligently the above-mentioned problem and found that it can not be solved by thoroughly washing with water the shaped article in the gelled state. The present invention is intended to solve the above-explained problems and is characterized in that a shaped article in a gelled state, which is obtained by introducing a solution of a poly-1,3,4-oxadiazole resin in

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- concentrated sulfuric acid into a coagulating bath to be coagulated and then washing the coagulated articles if necessary, is brought into contact with at least one aqueous solution which is
- (1) A buffer solution having a pH between 5 and 12,
 - (2) an aqueous solution of an amide compound soluble in water,
 - (3) an aqueous solution of an amide, or
 - (4) an aqueous solution of a hydroxide, carbonate, bicarbonate, silicate, acetate or phosphate of sodium, potassium, lithium, magnesium, copper, manganese or zinc,
- and then washed chiefly with water and dried whereby a shaped article having an improved dimensional stability, lowered water and moisture absorption properties and an improved thermal stability for a long period of time at, for example, 150°—200° C. can be obtained without degradation of other properties. Furthermore, it has been found that additional effects which vary depending upon the treating agents, can be attained by such a treatment; for example, the electric properties and light resistance may be improved.
- The reason why such properties are improved by causing a shaped article in gelled state to be in contact with the solutions (1)—(4) described above it believed to be as follows.
- A 1,3,4-oxadiazole ring contained in the recurring unit of poly-1,3,4-oxadiazole resin is basic and is protonized in a sulfuric acid solution to form strong positive ions. These positive ions are very stable and remains stable in water without being decomposed during coagulation and permit the polymer molecules to expand by their mutual repulsion and further make the degree of swelling large by their hydration. For these reasons, it is believed that the shaped article has, even after drying, a high rate of water absorption, a poor dimensional stability and a low heat resistance. In the shaped article in the gelled state of this invention, the positive ions are neutralized and consequently the polymer is aggregated by the above-noted treatment, so that the shaped article after drying is caused to have a low rate of water absorption, a good dimensional stability, high mechanical strength and a high heat resistance. Moreover, in spite of the fact that poly-1,3,4-oxadiazole resins have a tendency to absorb easily not only protons but also positive metal ions, by such treatment, ions having adverse effects on poly-1,3,4-oxadiazole resins, e.g. iron ions and calcium ions contained in the sulfuric acid and water respectively and concentrated in the shaped article, are replaced by ions capable of being removed by water washing. In a polymer such as a polybenzimidazole
- and a polyamide which is known to be capable of wet-shaping by using sulfuric acid, it is unnecessary to use the above-mentioned treatment. In contrast, in this invention such treatment is indispensable for poly-1,3,4-oxadiazole resins due to their characteristics. As the poly-1,3,4-oxadiazole resin useful in the present invention there can be used a polymer which contain a 1,3,4-oxadiazole ring and an aromatic ring or aromatic rings with or without heterocycles and, if necessary, —CH₂—, O—O—, —S—, —CO—, and SO₂, in the recurring unit, and include a polymer containing N-alkyl hydrazide groups in place of some of the 1,3,4-oxadiazole rings of the above-mentioned polymer, said N-alkyl hydrazide being less than 50 mol % of the polymer in the recurring unit of the above-mentioned polymer.
- Examples of said resins include poly (p-phenylene-1,3,4-oxadiazole) and polymers in which the p-phenylene unit of poly (p-phenylene-1,3,4-oxadiazole) is partially or entirely replaced by m-phenylene, oxybiphenylene, carbonylene biphenylene, sulfonylene biphenylene, 2,2' - biphenylene - bibenzimidazole, 2,2' - biphenylene-dibenzoxazole, 2,5' - biphenylene-1,3,4-thiadiazole, bisindro [1,2-a] quinazole dione-6,6'-ylene.
- N-alkyl hydrazide groups which may replace some of the 1,3,4-oxadiazole rings includes N-methyl ethyl, isopropyl and isobutyl hydrazide groups. The method of this invention is most significantly used for resins containing p-phenylene or p/m-phenylene units and 1,3,4-oxadiazole rings which, of all poly-1,3,4-oxadiazole resins, is most liable to protonation though excellent in various properties.
- The concentrated sulfuric acid used as the solvent for the poly-1,3,4-oxadiazole resin in this invention has a concentration of 78 to 110% by weight, preferably 90 to 106% by weight, most preferably about 100% by weight.
- The concentration of the resin in the resin solution and the molecular weight of the resin are closely related to the viscosity of the solution. The viscosity of the solution is important in wet-shaping processes. In this invention, it is preferable that the viscosity is as high as possible. The concentration of a resin can be properly selected in consideration of the desired properties of the shaped articles for which it is used and also the shaping quality of its solution, which however may ordinarily be from 2% to 15% by weight. It is necessary that the inherent viscosity of the resin, corresponding to its molecular weight, is more than 0.4 in the case of a resin containing no N-alkyl hydrazide bonds and more than 0.04 in the case of a resin containing said bonds, preferably more than 1.4 in the former case and more than 0.4 in the latter case in order that the resultant

shaped articles may have excellent mechanical properties and heat resistance. In order to improve the properties of the shaped articles of said resin, for example, mechanical properties, light resistance, or inflammability, fillers may be added to a solution of poly-1,3,4-oxadiazole resins. They include, for example, carbon black, carbon fiber, glass fiber, glass beads, glass balloon, silica, and alumina powder.

A solution of a poly-1,3,4-oxadiazole resin in concentrated sulfuric acid may be coagulated by wet-shaping process in a coagulating bath as proposed in publicly disclosed German Patent Application 1,769,151 and in British Patent Specification 1,252,508 as follows:—

(A) 15 to 68% by weight aqueous solution of sulfuric acid,

(B) 60 to 100% by weight aqueous solution of lower aliphatic carboxylic acid having pK_a (25° C.) of less than 3.8,

(C) mixed aqueous solution of sulfuric acid and at least one of the above carboxylic acids, in which the quantity of sulfuric acid is 15 to 68% by weight or in which the quantity of said carboxylic acids is more than 60% by weight, and

(D) a solution of any one of the above-described coagulating baths (A) to (C) mixed with less than saturated concentration of at least one sulfate, phosphate, chloride or nitrate of aluminium, sodium, zinc, magnesium, nickel, copper, potassium or manganese.

Furthermore, the following solutions may be used.

(E) mixed solution of any one of the above-described coagulating baths (A) to (D) and amide compounds, for example, formamide, NN-dimethylformamide, acetamide, and N-methylpyrrolidone, and

(F) aqueous solution of zinc chloride, zinc sulfate, and zinc nitrate.

Shaped articles in a gelled state in the present invention—the gelled state means a state in which shaped articles are swollen chiefly with sulfuric acid and water or with water—can be obtained by extruding the above-described resin solution through proper shaping means, for example orifices having a desired cross-section, e.g. circular hole, rectangular slit, wave like slit and then introducing the thus extruded material into any one of the coagulating baths (A) to (F) to coagulate it or by impregnating with said resin solution glass cloths or inorganic porous material inert to the resin solution, for example, asbestos or rock wool articles and then dipping the impregnated glass cloths or inorganic porous materials in said coagulating bath to coagulate it, preferably by washing the coagulated matter with water, which makes it possible to shorten the time required for the subsequent treatment in which shaped articles in gelled state are brought into con-

tact with the below-mentioned aqueous solutions.

One of the following aqueous solutions can be used as a treating agent for contacting with the shaped article in the gelled state after being coagulated and preferably washed with water, in order to improve the properties of the shaped article:—

(1) buffer solutions having a buffer action within a pH range of 5.0 to 12.0. Among them, the use of Clark-Lubs' buffer solution, Sørensen's buffer solution, Atkins-Pantin's buffer solution, Menzel's buffer solution and Comori's buffer solution is preferable.

(2) aqueous solutions of water-soluble acid amides, for example, formamide, N-methyl (or ethyl, propyl, butyl) formamide, N,N-dimethyl (or diethyl, dipropyl, dibutyl) formamide, acetamide, N,N-dimethyl (or diethyl) acetamide, diacetamide, triacetamide, methylene-diacetamide, propionamide, oxalic amide, N-methyl pyrrolidone. Among them, the use of formamide, N,N-dimethyl formamide, N,N-diethyl formamide, N,N-dimethyl acetamide, acetamide and N-methyl pyrrolidone is preferable in view of their affinity for the shaped article and high solubility in water.

(3) aqueous solutions of amines, for example, butylamine, propylamine, diethylamine, triethylamine, ethylenediamine, trimethylenediamine, nonmethylenediamine, piperazine, hexamethylenetetramine, ethanalamine, diethanalamine, triethanalamine, morpholine, N-methylmorpholine, p-aminophenol, aniline, ethylaniline, dimethylaniline, toluidine, pyridine, o-phenylenediamine, α -naphthylamine. Particularly, in view of auxiliary effects, for example, a high penetration into the shaped article and a high solubility of the resulting sulfuric acid salt in water, monoethanalamine, diethanalamine, triethanalamine, aniline, triethylamine, pyridine and p-aminophenol are preferable.

(4) aqueous solutions of hydroxides, carbonates, bicarbonates, silicates, acetates and phosphates of sodium, potassium, lithium, magnesium, zinc, copper and manganese. In view of the auxiliary effect, the use of sodium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate and sodium silicate is preferable.

The treating agents are limited as described above for the following reasons. It should be expected that if only the neutralization of the remaining acid is aimed at, any one of basic substances can attain the same effect as mentioned above, but as a matter of fact, it has been confirmed that basic substances other than the above defined substances degrade various properties of the shaped articles and bring about negative effects.

In order to contact the shaped article in the gelled state, obtained by wet shaping process, with any of the above-mentioned aqueous solution for said treatment, there are

several procedures, including the one in which the shaped article is passed through or dipped into the aqueous solution and also the one in which the aqueous solution is sprayed on the shaped article. The present invention is not limited to these procedures.

The concentration of the aqueous solutions for said treatment is not critical, but it is usually less than 10%, preferably less than 5% because at a higher concentration the said solutions are unnecessarily adsorbed by the shaped articles of the poly-1,3,4-oxadiazole resins and water-washing after said treatment must be carried out for a long period of time. Furthermore, the temperature of the aqueous solutions is not critical.

If necessary, the resulting poly-1,3,4-oxadiazole resin shaped articles coagulated in the above-described coagulating bath are drawn preferably within a range of less than 15 times their original length in the gelled state or in the undried state, whereby the shaped articles having excellent transparency and mechanical properties particularly, can be obtained. In this case, the drawing can be effected in a wet state containing either the coagulating solution or the washing water and further such drawing can be effected in a liquid coagulating bath, e.g. of water or glycerine or in air.

The drawing temperature has also a wide range and as far as the shaped articles are in undried state, there is no limitation in any condition. Furthermore, the shaped articles obtained in a coagulating bath can be drawn somewhat even in a dried state. This can be seen apparently from the fact that the shaped articles under the present invention have a large value of elongation at break.

Poly-1,3,4-oxadiazole resin shaped articles obtained by the present invention, with or without drawing, can be given an improvement in chemical and thermal resistance and other properties, for example, moisture absorption and dimensional stability by heating, for example, at 200° C. to 600° C.

The invention will be further explained in detail by the following Examples. The parts and percentages are by weight.

Example 1.

332 parts of terephthalic acid, 264 parts of hydrazine sulfate and 5300 parts of fuming sulfuric acid containing 23.4% of SO₃ were charged into a reaction vessel, and the resulting mixture was reacted at 130° C. for 4 hours to obtain a solution of poly (p-phenylene-1,3,4-oxadiazole) in fuming sulfuric acid having a viscosity of 13,100 poises at 30° C. The resulting polyoxadiazole resin had an inherent viscosity of 4.5 in 0.3% resin solution in 100% sulfuric acid at 30° C.

This resin solution was extruded through a spinneret provided with 15 orifices, each 0.2 mm diameter, into 54% aqueous solution

of sulfuric acid at 26° C. and coagulated into a filament. The filament obtained was introduced into a water bath to remove most of sulfuric acid for 10 minutes, thus being turned into a gelled state, fully swollen with water. It was then led into a bath of an aqueous solution of sodium hydroxide (0.5 weight % concentration), and further into a water bath to wash, and drawn to 3 times its original length and then dried. The resulting filaments had a fineness of 7.2 deniers, a tenacity of 4.2 g/denier, an elongation at break of 50% and a Young's modulus of 72 g/denier. Also the filaments had a moisture absorption of 6.4% at 80% RH at 20° C. This filament did not show any change of tenacity after heating at 350° C. in air for 10 hours, and after heating at 200° C. in air for 5,000 hours.

For comparison, the filament obtained by the same manner as described above, except that the treatment with the aqueous solution of sodium hydroxide was not effected, had a moisture absorption of 12.7% at 80% RH at 20° C. and showed 12% decrease of its original tenacity after heating at 200° C. in air for 5,000 hours. It did not show any change of tenacity after heating at 350° C. in air for 10 hours.

Example 2.

Into a reaction vessel were charged 1,040 parts of 4,4'-dicarboxydiphenyl ether, 550 parts of hydrazine sulfate and 7,930 parts of fuming sulfuric acid containing 18.3% of SO₃ and the mixture was reacted at 130° C. for 6 hours while being stirred to obtain a solution of poly 4,4'-oxy-diphenylene-1,3,4-oxadiazole in fuming sulfuric acid. The synthesized polyoxadiazole resin had an inherent viscosity of 2.46 in 0.3% solution of 100% sulfuric acid at 30° C.

The solution of polyoxadiazole in fuming sulfuric acid thus obtained was diluted with 100 parts of 98% sulfuric acid and stirred thoroughly to make the concentration of sulfuric acid 100%, the concentration of resin 14%, and the solution viscosity of 4,000 poises.

The resin solution thus obtained was poured onto a glass plate, dipped for one minute in the same coagulation bath as described in Example 1 and for 5 minutes in a water bath at 25° C., thus being turned into a gelled state, containing some sulfuric acid. It was then put for one minute in a bath of an aqueous solution of sodium bicarbonate (7 weight % concentration), and further for 10 minutes in a running water bath.

The film thus obtained was in gelled state and swollen by water 4.6 times as much as the weight of polyoxadiazole in an absolutely dried state. The dried film has a tensile strength of 1040 kg/cm² and an elongation of 124%.

For comparison, the film was produced in the same procedure as described above, except that the treatment with the aqueous solution of sodium bicarbonate was not effected, and said resulting film was in a gelled state and swollen by water 6.1 times as much

as the original weight and had substantially the same tensile strength, and elongation at break, but after heating at 180° C. for 4 weeks, their values decreased as shown in the following table.

| | Tensile strength | Elongation at break |
|------------|-------------------------|---------------------|
| Example | 1050 kg/cm ² | 48% |
| Comparison | 920 kg/cm ² | 16% |

Example 3.

The polyoxadiazole resin solution used in Example 1 was extruded through a spinneret with 30 orifices, each 0.075 mm in diameter, into a coagulating bath at 20° C. containing 45% aqueous solution of sulfuric acid, in which 12% magnesium sulfate was dissolved, to obtain continuous filaments at a velocity of 10 m/min.

The filament was drawn to 5 times its original length and washed with water. The

filament in a gelled state thus obtained was then immersed into an aqueous solution of aniline (1 weight % concentration) and further washed with water and then dried and heat-treated at 340° C. for 5 minutes.

For comparison, a filament was produced in the same manner as described above except that the treatment with the aniline solution was not effected. The properties of two kinds of the filaments were as follows.

| | Example | Comparison |
|----------------------------------------|---------|------------|
| Initial fineness (den.) | 2.8 | 2.8 |
| tenacity (g/den.) | 4.6 | 4.2 |
| elongation at break (%) | 20 | 18 |
| Young's modulus (g/den.) | 98 | 88 |
| moisture absorption (80% RH, 20°C) (%) | 4.7 | 10.3 |
| After aging at 180°C for 3 months | | |
| fineness (den.) | 2.8 | 2.8 |
| tenacity (g/den.) | 4.6 | 4.1 |
| elongation at break (%) | 18 | 13 |
| Young's modulus (g/den.) | 102 | 92 |
| After outdoor exposure for a month | | |
| fineness (den.) | 2.8 | 2.8 |
| tenacity (g/den.) | 4.6 | 3.7 |
| elongation at break (%) | 14 | 8 |
| Young's modulus (g/den.) | 99 | 92 |

Example 4.

141.10 parts of terephthalic acid, 24.9 parts of isophthalic acid, and 132 parts of hydrazine sulfate were added to 2,100 parts of fuming sulfuric acid containing 20% of SO₃ and then the resulting mixture was reacted at 130° C. for 4 hours to obtain a solution of poly p-/m-phenylene-1,3,4-oxadiazole copolymer (p/m ratio: 85/15) in fuming sulfuric acid.

The viscosity of the solution was 9,350 poises and the inherent viscosity of the co-

polymer in 100% sulfuric acid was 3.26.

The solution of the copolymer thus obtained was extruded through a slit having a width of 0.5 mm onto a moving TEFLON (Registered Trade Mark) impregnated glass cloth and coagulated by continuously passing it through a coagulating bath containing a 65% aqueous solution of sulfuric acid for 20 seconds and through a 30% aqueous solution of sulfuric acid for 25 seconds and then introduced into a water bath. After being washed with water, the gelled state film was

- peeled off the glass cloth, immersed in a 1% aqueous solution of monoethanolamine for 1 minute, and then thoroughly washed with water and dried and further heat-treated at 400° C. for 1 minute.

The properties of the film thus obtained

are shown in the following table. For comparison, the properties of the film obtained in the same manner as described above except that the treatment with the monoethanol amine solution was not effected are also shown in the table.

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| | Example | Comparison |
|---------------------------------------------|--------------------------|--------------------------|
| Density | 1.40 | 1.39 |
| Strength | 1,480 kg/cm ² | 1,460 kg/cm ² |
| Elongation | 40% | 42% |
| Electric resistance | 190 V/mm | 162 V/mm |
| $\tan \delta$ | 0.002 | 0.004 |
| ϵ | 3.1 | 3.3 |
| Moisture absorption (80% RH, 20°C) | 2.3 % | 6.2 % |
| Dimensional change after immersion in water | 0.4 % | 0.8 % |
| After heating at 200°C for 6,000 hours | | |
| Strength | 1,420 kg/cm ² | 860 kg/cm ² |
| Elongation | 11.2 % | 2.6 % |

Example 5.

- 15 Into a reaction vessel were charged 1209 parts of terephthalic acid, 955 parts of hydrazine sulfate and 15350 parts of fuming sulfuric acid containing 17% of SO₃. The resulting mixture was reacted at 130° C. for 20 4 hours while being stirred to obtain poly (p-phenylene-1,3,4-oxadiazole), which had an inherent viscosity of 2.86 in a 0.3% solution in 100% sulfuric acid at 30° C. The resin solution (concentration of resin 6%, concentration of sulfuric acid 101%, solution viscosity 3870 poises at 30° C.) thus prepared was extruded through a slit having a width of 0.5 mm and a length of 500 mm onto a polyethylene sheet 200 μ thick which was moved through a coagulation bath of 53% aqueous sulfuric acid at 20° C. at a velocity of 1 m/min.

- 30 After coagulation, sheet-shaped polyoxadiazole was immersed in a washing bath for 5 minutes thus being turned into a water-swollen gelled state, and then into a 1% sodium

hydroxide for 2 minutes and further in a water bath for 10 minutes.

The shaped article in gelled state was dried by being run through hot rollers at 150° C. and heat-treated at 400° C. for 2 minutes to obtain a polyoxadiazole film.

This film had a moisture absorption of 1.5% of the weight of absolutely dried film at 80% RH at 20° C. and had a good dimensional stability after immersion in hot water.

For comparison, the film obtained by the same process described above, except that the sodium hydroxide bath was not used, had the moisture absorption of 3.7% of the weight of absolutely dried film, and the dimensions of the film were increased by 1.6% of the original length and width after immersion in hot water. The following table shows the tensile properties of the films obtained by the two processes described above.

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| | Example | Comparison |
|-------------------------------------|-------------------------|-------------------------|
| Tensile strength | 1270 kg/cm ² | 1240 kg/cm ² |
| Elongation | 54% | 62% |
| After heating at 200°C for 2 months | | |
| Tensile strength | 1270 kg/cm ² | 1160 kg/cm ² |
| Elongation | 38% | 12% |

Example 6.

285 parts of terephthalic acid, 95 parts of isophthalic acid, 314 parts of hydrazine sulfate and 4000 parts of fuming sulfuric acid containing 30% of SO₃ and 20 parts of methanol were reacted at 90° C. for 2 hours while being stirred in a reaction vessel and then the temperature was raised to 130° C. and the reaction was continued for about 4 hours to obtain a solution of 1,3,4-oxadiazole-N-methylhydrazide copolymer (1,3,4-oxadiazole units 88 mol %, N-methylhydrazide units 12 mol %) in fuming sulfuric acid. The inherent viscosity of the resulting 1,3,4-oxadiazole-N-methylhydrazide copolymer was 0.41 in 0.3% solution in 100% sulfuric acid at 30° C.

This solution was extruded through a slit having a width of 0.3 mm and a length of 100 mm into a coagulating bath containing 35% aqueous solution of sulfuric acid at 40° C. and having a length of 1 m and coagulated into a film. It was then washed with water to form a water-swollen gel and passed through a bath of 2% sodium carbonate aqueous solution with five stages of guide rollers at a velocity of 3 m/min. The resulting film was immediately drawn to 1.5 times its original length in a hot water at 60° C., and then washed with water and dried. The thus produced film, 0.025 mm in thickness, had a tensile strength of 1,630 kg/cm² and an elongation at break of 18%. This film retained the original tensile strength after heat aging tests at 220° C. for 240 hours and also at 180° C. for 5,000 hours. But the film which was not passed through a bath of 2% sodium carbonate aqueous solution retained only 80% of the original tensile strength after heat aging test at 180° C. for 5,000 hours.

Further, two films obtained above were compared with each other as to dimensional stability with the following results.

Example 0.26% (after immersion in water at 30° C.) 45
Comparison 0.72% (after immersion in water at 30° C.)

Example 7.

Into a reaction vessel were fed 249 parts of terephthalic acid, 97 parts of dimethyl isophthalate, 273 parts of hydrazine sulfate and 2,400 parts of fuming sulfuric acid containing 20% of SO₃ and the resulting mixture was reacted while being stirred at 130° C. for 6 hours to obtain a solution of 1,3,4-oxadiazole-N-methylhydrazide copolymer (1,3,4-oxadiazole units 86 mol %, N-methylhydrazide units 14 mol %) in fuming sulfuric acid. The resulting copolymer had an inherent viscosity of 0.48 in 0.3% solution in 100% sulfuric acid at 30° C. Then, the resulting solution of the copolymer in fuming sulfuric acid was diluted with 600 parts of 90% sulfuric acid and stirred thoroughly to decrease the viscosity of the solution (concentration of sulfuric acid 98%, concentration of resin 8% and solution viscosity 2,300 poises). The resin solution thus produced was extruded through a spinneret provided with 30 orifices, each 0.075 mm in diameter, into 20% aqueous solution of sulfuric acid containing 16% of ammonium sulfate at 45° C. and coagulated into a filament at a linear velocity of 21 m/min. and the filament thus obtained was treated in the same manner as described in Example 1. For comparison, the spinning was effected in the same manner as described above except that an aqueous solution of ferric hydroxide (1% by weight concentration) was used in place of the aqueous solution of sodium hydroxide.

The properties of the resulting filaments were as follows.

| | Example | | | Comparison | | |
|----------------------|---------|---------------------------------------|---------------------------------------|------------|---------------------------------------|---------------------------------------|
| Water absorption (%) | 10.2 | | | 28.6 | | |
| | Initial | After heating at 180°C for 2000 hours | After outdoor exposure for 1000 hours | Initial | After heating at 180°C for 2000 hours | After outdoor exposure for 1000 hours |
| T | 4.1 | 4.8 | 4.0 | 3.5 | 2.3 | did not measure |
| E | 42 | 29 | 25 | 12 | 5 | |
| Y | 57 | 82 | 75 | 55 | 67 | |

T: tenacity (g/den.), E: elongation at break (%),
Y: Young's modulus (g/den.).

Example 8.

5 The same resin solution as that used in Example 5, to which was added 4% of sodium sulfate, was poured onto a glass plate, dipped for 1 minute in a 10° C. coagulating bath containing 30% aqueous solution of sulfuric acid, and washed with water for 30 minutes, thus being turned into a gelled state film swollen with water. It was then immersed into a Menzel's buffer solution (pH 9.9) consisting of the mixture of 0.2 mole sodium carbonate and 0.2 mole sodium bicarbonate in 2 liters of water and washed again with

water to obtain light yellow and translucent swollen film. Then, the resulting film while wet was subjected to bi-axial drawing, that is, twice as large in the longitudinal direction and 1.5 times as large in the transverse direction, washed with water, and dried in the stretched state. The thus obtained film was light yellow and transparent.

For comparison, another film was obtained in the same manner as described above, except that Menzel's buffer solution treatment was omitted. The properties of the resulting films were as follows.

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| | Example | | | | |
|---------------------------------------------------------|---------|----------------------------|----------|----------|------------------------------------|
| Density | 1.38 | | | | |
| Weight increase after immersion in water for 5 days (%) | 4.6 | | | | |
| Elongation after immersion in water (%) | 0.42 | | | | |
| | Initial | After heating at 180°C for | | | After outdoor exposure for 1 month |
| | | 1 month | 2 months | 3 months | |
| TS | 16.8 | 16.9 | 16.9 | 16.9 | 16.8 |
| E | 25 | 22 | 21 | 21 | 25 |

| | Comparison | | | | |
|---------------------------------------------------------|------------|----------------------------|----------|----------|------------------------------------|
| Density | 1.36 | | | | |
| Weight increase after immersion in water for 5 days (%) | 17.3 | | | | |
| Elongation after immersion in water (%) | 1.7 | | | | |
| | Initial | After heating at 180°C for | | | After outdoor exposure for 1 month |
| | | 1 month | 2 months | 3 months | |
| TS | 16.8 | 16.8 | 16.7 | 16.6 | 14.3 |
| E | 30 | 19 | 14 | 12 | 7 |

TS: tensile strength (kg/mm²)

E: elongation at break (%)

Example 9.

2 parts of propylene were absorbed under pressure in 200 parts of 4% polyoxadiazole solution in 100% sulfuric acid obtained by diluting the solution obtained in Example 1. The resulting mixture was reacted at 30° C. for 2 hours to obtain a solution of N-isopropylhydrazide-1,3,4-oxadiazole copolymer (N-isopropylhydrazide units 23%, 1,3,4-oxadiazole units 77%) (inherent viscosity 0.54) in sulfuric acid. This resin solution having a viscosity of 4,400 poises was extruded through a spinneret with 30 orifices, each 0.075 mm in diameter, into a 59% aqueous solution of sulfuric acid, to which was added 8% of magnesium sulfate, and coagulated at 60° C. and at a linear velocity of 5.8 m/min. The resulting filament in a gelled state was repeatedly drawn 10 times, each time to a length 1.1 times as large as the previous length, washed with water and dried. This drawing was made 3 times in water, 2 times in a bath consisting of 1% concentration of pyridine in water, 3 times in water and 2 times in 80° C. hot water. The resultant filament was swollen by water 3.7 times as much as the original weight of filament. Then the filament was passed through a furnace at 350° C. for 2 minutes to obtain yellow filament having a fineness of 2.2 den., a tenacity of 4.2 g/den., an elongation at break of 32% and a Young's modulus of 85 g/den. Even after the filament was dipped in 10% aqueous alkali solution or 30% aqueous strong mineral acid solution for 48 hours, the tenacity was not changed. Moreover even after the filament was heated at 250° C. for 24 hours in air, their mechanical properties were not substantially changed. When the above spun filament was not heat-treated in a furnace at 350° C., it was soluble in 10% aqueous alkali solution.

For comparison, the filament obtained in the same manner as described above except that a water bath was used in place of an aqueous pyridine solution bath, was in a gelled state and swollen by water 5.4 times as much as its original weight of filament. The dried filament decreased to 12% in tenacity after heating at 200° C. for 5,000 hours although the filament in this example did not show any change in tenacity after the same heat aging.

Example 10.

The same resin solution as used in Example 1 was poured on a glass plate and dipped into 98% formic acid at 10° C. to obtain a film in a gelled state with a sulfuric acid content and having a thickness of 0.200 mm. This film was washed with 20% aqueous solution of formic acid and then thoroughly washed with water to form a water-swollen gel, immersed into Sørensen's buffer solution (pH 6) consisting of KH_2PO_4 and Na_2HPO_4 and thoroughly washed with water again, sub-

jected to bi-axial drawing to 1.5 times its original length and dried to obtain a translucent film, which had a tensile strength of 1,680 kg/cm², and an elongation at break of 6%. This film had a moisture absorption of 1.7% and a dimensional change of 0.96% after immersion in water. The film, after being heated at 250° C. for 1,000 hours and at 180° C. for 10,000 hours, had a tensile strength of 1,620 kg/cm² and an elongation at break of 5% showing substantially no change.

For comparison, the filament obtained in the same manner as described above, except that Sørensen's buffer solution consisting of glycine, sodium chloride and sodium hydroxide (pH 12.60 at 20° C.) was used in place of buffer solution used in this example, had a moisture absorption of 4.7% and a dimensional change of 4.2% after immersion into water. This filament decreased in tensile strength to 92% of its original value after heating at 180° C. for 10,000 hours.

Example 11.

The same resin solution as the one used in Example 1 was extruded through a spinneret with 15 orifices, each 0.200 mm in diameter, into a coagulating bath containing 78% aqueous solution of formic acid, to which was added 7% of zinc chloride, and having a length of 500 cm to obtain a filament at 21° C. at a take-up velocity of 18 m/min. The filament was drawn to 4.3 times its original length, washed with water, thus being turned into a gel swollen with water, immersed in a bath consisting of 5% concentration of N_2N -dimethylformamide in water and thoroughly washed with water and dried to obtain a yellowish white filament. The resulting filament had a fineness of 3.4 den., a tenacity of 3.8 g/den., an elongation at break of 11%, a Young's modulus of 48 g/den. and a water absorption of 12.4%.

The filament obtained in this example and the filament obtained in the same manner as described above except that the treatment with N_2N -dimethylformamide solution was not effected for comparison, were heat-aged at 200° C. for 3,000 hours. The retention of tenacity after aging was 98% of initial value in the former, 62% in the latter, respectively. The water absorption in the latter was 30.4%.

Example 12.

194 parts of isophthalic dihydrazide, 295 parts of 4,4'-oxy-di-(benzoyl chloride) were stirred vigorously in 2,000 parts of hexamethylphosphoramide for 24 hours while the reaction temperature was kept at lower than 15° C. to obtain a viscous milk-white solution, which was poured into a large amount of water, whereby resin was precipitated. The resulting resin was washed with water thoroughly and then dried at 100° C. under vacuum to obtain polyhydrazide resin. This polyhydrazide

resin was heated at 280° C. under vacuum to effect cyclodehydration, whereby m-phenylene-4,4'-oxydiphenylene-1,3,4-oxadiazole copolymer was obtained. This polyoxadiazole resin was dissolved in 100% sulfuric acid to obtain a solution having a polyoxadiazole resin concentration of 12% and a solution viscosity of 2,900 poises. (The resulting polyoxadiazole resin had an inherent viscosity of 1.60 in 0.3% resin solution in 100% sulfuric acid at 30° C.).

A glass cloth was impregnated with the resin solution thus obtained, then dipped for 1 minute into a 40° C. coagulating bath composed of an aqueous solution containing 25% of sulfuric acid and 10% of nitric acid, and then washed with water, dipped in 2% morpholine aqueous solution for 5 minutes, washed again with water and dried.

The yellowish white impregnated glass cloth contained 39% of resin and moisture absorption of 0.4% of the weight of absolutely dried glass cloth and had a dielectric strength of 48 KV, a volumetric resistivity of 10^{15} Ω cm, a dielectric constant of 4.2 and a $\tan \delta$ of 0.32%.

For comparison, the impregnated glass cloth obtained in the same manner as described above except that the treatment with the morpholine solution was not effected, had a moisture absorption of 1.7% of absolutely dried glass cloth, a dielectric strength of 45 KV, a volumetric resistivity of 10^{14} Ω cm, a dielectric constant of 4.2, and $\tan \delta$ of 4.5%.

After heating at 200° C. for 5,000 hours, the dielectric strengths of the impregnated glass cloth obtained in this example and in comparison were 48 KV and 37 KV, respectively.

Example 13.

The same resin solution as the one used in Example 4 was extruded through a spinneret with 10 orifices, each 0.075 mm in diameter, into 65% aqueous solution of dichloroacetic acid at 20° C. at a velocity of 12 m/min. to obtain a filament in a gelled state with a high sulfuric acid content. Immediately after the filament was dipped in 8% lithium hydroxide aqueous solution for 10 minutes, it was drawn to 2 times its original length in a running water bath and dried at 210° C.

The filament thus obtained had a fineness of 4.5 den., a tenacity of 2.3 g/den., an elongation at break of 9%, a Young's modulus of 52 g/den. and a moisture absorption (RH 80%, 20° C.) of 2.7% and did not change in tenacity after heating at 210° C. in air for 500 hours. But the tenacity of a filament obtained in the same manner as described above except that the treatment with the aqueous solution of lithium hydroxide was not effected, decreased by 7% of its initial value after heating under the same condition as de-

scribed above. The filament had a moisture absorption (RH 80%, 20° C.) of 7.6%.

Example 14.

28 parts of 2 - (p - carboxyphenyl) - 5(6)-carboxy benzoxazole, 149 parts of terephthalic acid and 138 parts of hydrazine sulfate were dissolved in 4,000 parts of fuming sulfuric acid containing 25% of SO_3 and the resulting solution was reacted in the same manner as described in Example 2 to obtain a resin solution having an inherent viscosity of 2.98 in concentrated sulfuric acid.

The resin solution was diluted with 95% sulfuric acid so as to make the concentration of sulfuric acid 100%, poured on a glass plate, dipped in a 45% aqueous solution of sulfuric acid at 38° C. for coagulation, washed with water to form a water-swollen gel, immersed for 3 minutes in 1% triethanolamine aqueous solution, washed again with water and dried at 100° C. to obtain a film. This film had a tensile strength of 1,850 kg/cm², an elongation at break of 35% and a moisture absorption (80% RH, 20° C.) of 1.7%. After heating at 400° C. for 1 minute, the film had a tensile strength of 1,970 kg/cm² and an elongation at break of 27% and did not change in tensile strength and retained the elongation of 18% after heating at 200° C. for 1 month.

For comparison, the film obtained in the same manner as described above, except that the coagulated film was not immersed in the aqueous solution of triethanolamine but was washed with water for 24 hours and dried at 100° C., had the moisture absorption (80% RH, 20° C.) of 3.8% and did not show any change in its initial value as in the above case, but showed somewhat deteriorated mechanical properties after heating at 200° C. for 1 month, i.e., the tensile strength was 1,840 kg/cm² and the elongation was 12%.

Example 15.

A copolymer of benzimidazole and 1,3,4-oxadiazole obtained by reacting 2,2' - di-(4-carboxyphenyl) - 5,5' - bi - benzimidazole with hydrazine sulfate in polyphosphoric acid (inherent viscosity 2.00, measured in the same manner as described in Example 1) was dissolved in 100% sulfuric acid so as to make the resin concentration 8.2%. The resin solution was extruded through a spinneret having 30 orifices of 75 μ in diameter into a 45% aqueous solution of sulfuric acid containing 10% of manganese sulfate and the resulting coagulated filament, while being passed at a rate of 5.8 m/min., was washed with water, thus being turned into a water-swollen gel, immersed for 5 minutes in a buffer solution consisting of boric acid, potassium chloride and sodium hydroxide and having a pH of 9.6 (Clark-Lubs' buffer solution), washed again with water and dried. The resulting

filament was heated at 390° C. for 1 minute.

The properties of the filament thus obtained are shown in the following table. Moreover, for comparison, a filament was obtained in the same manner as described above except

that the coagulated filament was not immersed in the Clark-Lubs' buffer solution and was washed with water for 24 hours, and the properties thereof are also shown in the table.

| | Example | Comparison |
|-----------------------------------------------------------|---------|------------|
| Fineness (denier) | 3.9 | 3.9 |
| Strength (g/denier) | 5.4 | 5.4 |
| Elongation (%) | 18 | 15 |
| After heating at 200°C for 1 month Strength (g/denier) | 5.4 | 5.1 |
| After heating at 200°C for 1 month Elongation (%) | 17 | 11 |
| After outdoor exposure for 1 month Strength (g/denier) | 5.4 | 3.6 |
| After outdoor exposure for 1 month Elongation (%) | 14 | 4.7 |
| Moisture absorption (%) | 2.6 | 5.8 |
| Dimensional stability (%/% RH at 30°C) | 0.012 | 0.056 |

WHAT WE CLAIM IS:—

1. A method for producing a shaped article of a poly-1,3,4-oxadiazole resin having improved properties, characterized in that the shaped article in a gelled state, which is obtained by introducing a solution of a poly-1,3,4-oxadiazole resin in concentrated sulfuric acid into a coagulating bath to be coagulated and then washing the coagulated article, if necessary, is brought into contact with at least one aqueous solution which is

- (1) a buffer solution having a pH from 5 to 12
- (2) an aqueous solution of an amide compound soluble in water
- (3) an aqueous solution of an amine or
- (4) an aqueous solution of a hydroxide, carbonate, bicarbonate, silicate, acetate or phosphate of sodium, potassium, lithium, magnesium, copper, manganese or zinc

and then washed and dried.

2. A method as claimed in claim 1 wherein said poly-1,3,4-oxadiazole resin is poly(p-phenylene - 1,3,4 - oxadiazole) or poly(p-/m-phenylene - 1,3,4 - oxadiazole).

3. A method as claimed in claim 1 wherein said buffer solution is Clark-Lubs', Sørensen's, Atkins-Pantin's, Menzel's or Comori's buffer solution having a pH from 5.0 to 12.0.

4. A method as claimed in claim 1 wherein said amide compound is formamide, N,N-dimethyl or diethyl formamide, acetamide, N,N-dimethyl or diethyl acetamide or N-methyl pyrrolidone.

5. A method as claimed in claim 1 wherein said amine is monoethanolamine, diethanolamine, triethanolamine, aniline, triethylamine, pyridine or p-aminophenol.

6. A method as claimed in claim 1 wherein said hydroxide, carbonate, bicarbonate, silicate or phosphate is sodium hydroxide, lithium hydroxide, sodium carbonate, potas-

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sium carbonate, sodium bicarbonate or sodium silicate.

5 7. A method as claimed in claim 1 further comprising drawing the shaped article in the gelled state or in the undried state produced by the method defined in claim 1.

10 8. A method as claimed in claim 1 further comprising heating the dried shaped article produced by the method defined in claim 1, at a temperature of 200° to 600° C.

15 9. A method as claimed in claim 1 further comprising drawing the shaped article in gelled state or in undried state produced by the method defined in claim 1 and then heating the drawn shaped article at a temperature of 200° to 600° C.

10. A method for producing a shaped article of a poly-1,3,4-oxadiazole resin having

improved properties substantially as hereinbefore described with reference to any one of the foregoing Examples. 20

11. A poly-1,3,4-oxadiazole resin film, fiber or impregnated material obtained by a process as claimed in claim 1.

12. A poly-1,3,4-oxadiazole resin film or fiber obtained by the processes as claimed in any one of claims 7, 8 and 9. 25

13. A poly-1,3,4-oxadiazole resin impregnated material obtained by the process as claimed in claim 8. 30

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